

Claims:

1. A method for making a molded calcium phosphate article comprising
impregnating a rigid shaped article of calcium phosphate with an impregnating
liquid for a period of time so that a compressive strength of the resulting
5 impregnated article removed from the impregnating liquid is increased compared
to that of said rigid shaped article without said impregnating treatment.

2. The method according to claim 1, wherein the impregnating liquid is an
acidic solution, a basic solution, a physiological solution, an organic solvent, or
10 a substantially pure water.

3. The method according to claim 2, wherein the impregnating liquid
comprises at least one of Ca and P sources.

15 4. The method according to claim 2, wherein the impregnating liquid is a
Hanks' solution, a HCl aqueous solution or an aqueous solution of $(\text{NH}_4)_2\text{HPO}_4$.

5. The method according to claim 1, wherein the rigid shaped article of
calcium phosphate is a molded article from a paste of calcium phosphate cement.
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6. The method according to claim 1, wherein the impregnating is carried
out for a period longer than 10 minutes.

7. The method according to claim 6, wherein the impregnating is carried
25 out for about 12 hours to 96 hours.

8. The method according to claim 1, wherein the impregnating is carried
out at room temperature or at a temperature between about 30 and 90°C.

30 9. The method according to claim 5, wherein said calcium phosphate
cement comprises one or more calcium phosphates selected from the group
consisting of alpha-tricalcium phosphate (α -TCP), beta- tricalcium phosphate

(β -TCP), tetracalcium phosphate (TTCP), monocalcium phosphate monohydrate (MCPM), monocalcium phosphate anhydrous (MCPA), dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA), octacalcium phosphate (OCP), calcium dihydrogen phosphate, calcium dihydrogen phosphate hydrate, acid calcium pyrophosphate, anhydrous calcium hydrogen phosphate, calcium hydrogen phosphate hydrate, calcium pyrophosphate, calcium triphosphate, calcium phosphate tribasic, calcium polyphosphate, calcium metaphosphate, anhydrous tricalcium phosphate, tricalcium phosphate hydrate, and amorphous calcium phosphate.

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10. The method according to claim 9, wherein the calcium phosphate cement comprises at least one calcium phosphate particle having calcium phosphate whiskers on the surface of said calcium phosphate particle, wherein said calcium phosphate whiskers have a length of about 1-5000 nm and a width of about 1-500 nm.

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11. The method according to claim 5, wherein said paste is formed by mixing said calcium phosphate cement with a setting liquid.

20 12. A method for making a molded calcium phosphate article comprising the following steps:

(a) preparing a powder comprising at least one Ca source and at least one P source, or at least one calcium phosphate source;

25 (b) mixing said powder with a setting liquid to form a paste, wherein said paste undergoes a hardening reaction;

(c) molding said paste into an article in a mold of a desired shape and size before said hardening reaction is complete;

(d) impregnating the resulting hardened article from step (c) with an impregnating liquid to allow strength of said article to increase; and

30 (e) removing said article from said impregnating liquid.

13. The method according to claim 12, wherein said calcium phosphate source in step (a) comprises one or more calcium phosphates selected from the group consisting of alpha-tricalcium phosphate (α -TCP), beta- tricalcium phosphate (β -TCP), tetracalcium phosphate (TTCP), monocalcium phosphate monohydrate (MCPM), monocalcium phosphate anhydrous (MCPA), dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA), octacalcium phosphate (OCP), calcium dihydrogen phosphate, calcium dihydrogen phosphate hydrate, acid calcium pyrophosphate, anhydrous calcium hydrogen phosphate, calcium hydrogen phosphate hydrate, calcium pyrophosphate, calcium triphosphate, calcium phosphate tribasic, calcium polyphosphate, calcium metaphosphate, anhydrous tricalcium phosphate, tricalcium phosphate hydrate, and amorphous calcium phosphate.

14. The method according to claim 12, wherein the calcium phosphate source comprises at least one calcium phosphate particle having calcium phosphate whiskers on the surface of said calcium phosphate particle, wherein said calcium phosphate whiskers have a length of about 1-5000 nm and a width of about 1-500 nm.

15. The method according to claim 12, wherein the setting liquid in step (b) is an acidic solution, a basic solution, or a substantially pure water.

16. The method according to claim 15, wherein said acidic solution is selected from the group consisting of nitric acid (HNO_3), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), carbonic acid (H_2CO_3), sodium dihydrogen phosphate (NaH_2PO_4), sodium dihydrogen phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), sodium dihydrogen phosphate dihydrate, sodium dihydrogen phosphate dehydrate, potassium dihydrogen phosphate (KH_2PO_4), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), malic acid, acetic acid, lactic acid, citric acid, malonic acid, succinic acid, glutaric acid, tartaric acid, oxalic acid and their mixture.

17. The method according to claim 15, wherein said basic solution is selected from the group consisting of ammonia, ammonium hydroxide, alkali metal hydroxide, alkali earth hydroxide, disodium hydrogen phosphate (Na_2HPO_4), disodium hydrogen phosphate dodecahydrate, disodium hydrogen phosphate heptahydrate, sodium phosphate dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), dipotassium hydrogen phosphate (K_2HPO_4), potassium hydrogen phosphate trihydrate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$), potassium phosphate tribasic (K_3PO_4), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), ammonium phosphate trihydrate ($(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), sodium hydrogen carbonate (NaHCO_3), sodium carbonate Na_2CO_3 , and their mixture.

18. The method according to claim 12, wherein step (c) further comprises removing said article from said mold.

19. The method according to claim 12, wherein step (c) further comprises removing a portion of liquid from said paste, so that a liquid/powder ratio of said paste decreases.

20. The method according to claim 12, wherein step (c) further comprises pressurizing said paste in said mold before said hardening reaction is complete to remove a portion of liquid from said paste, so that a liquid/powder ratio of said paste decreases.

21. The method according to claim 20, wherein step (c) further comprises heating said paste during said pressurizing.

22. The method according to claim 12, wherein step (c) further comprises heating said paste during molding.

23. The method according to claim 12, wherein step (d) further comprises heating the impregnating liquid during said impregnating.

24. The method according to claim 23, wherein step (d) further comprises heating the impregnating liquid at a temperature between about 30 and 90°C during said impregnating.

5 25. The method according to claim 12 further comprising drying said article after removing said article from said impregnating liquid.

26. The method according to claim 12 further comprising heating said article after removing said article from said impregnating liquid.

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27. The method according to claim 26, wherein said article after being removed from said impregnating liquid is heated at a temperature between 50 and 500°C.

15 28. The method according to claim 12, wherein the impregnating liquid in step (d) is an acidic solution, a basic solution, a physiological solution, an organic solvent, or a substantially pure water.

29. The method according to claim 28, wherein the impregnating liquid
20 comprises at least one of Ca and P sources.

30. The method according to claim 28, wherein the impregnating liquid is a Hanks' solution, a HCl aqueous solution or an aqueous solution of $(\text{NH}_4)_2\text{HPO}_4$.
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31. The method according to claim 12, wherein the impregnating in step (d) is carried out for a period longer than 10 minutes.

32. The method according to claim 31, wherein the impregnating is
30 carried out for about 12 hours to 96 hours.

33. The method according to claim 12, wherein the impregnating in step (d) is carried out at room temperature.